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A HAIR COSMETIC MATERIAL

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Claims

1. A cosmetic material for hair containing a fine particulate zeolite that contains at least one metal ion selected from the group of silver, copper, and zinc.

2. The cosmetic material for hair described in Claim 1 wherein the above-mentioned fine particulate zeolite is included in an amount of 0.001-50 wt% of the weight of the composition.

3. The cosmetic material for hair described in Claim 1 wherein the above-mentioned fine particulate zeolite has a specific surface area in the range of 150-1,000 m^2/g.

Detailed explanation of the invention

The present invention pertains to an improved cosmetic material for hair produced by mixing the specific type of fine particulate zeolite described below with a base for a cosmetic material for hair. More precisely, it further pertains to a cosmetic material for hair with antibacterial properties

(bactericidal action), antidandruff, anti-itching properties, and that provides easy combing and great texture.

Causes of dandruff and itching of the scalp are complex and are not well understood, but according to the literature, dandruff and itching increase with an increase in the presence of microbes on the scalp.

In the past, many different types of medications represented by colloidal sulfur, selenium sulfide, hydroxyquinoline, etc., have been used, but the effect, persistence, and safety of the above-mentioned medications have been inadequate.

As a result of research carried out by the inventors in an effort to improve the above-mentioned prior art, it was discovered that:

(1) a specific fine particulate zeolite described below does not irritate the skin and is safe for use on human beings.

(2) a cosmetic material for hair produced by mixing the specific fine particulate zeolite described below with a hair cosmetic base material has antibacterial properties (bactericidal action), antidandruff, anti-itching properties, and provides easy combing and a great texture, etc., and accomplished the present invention was accomplished.

That is, the present invention is a cosmetic material for hair containing fine particulate zeolite that contains at least one metal ion selected from silver, copper, and zinc.

In general, zeolite is an aluminosilicate with a structure that is developed in three dimensions and is commonly represented as:

$$XM_2/nO{\cdot}Al_2O_3{\cdot}ySiO_2{\cdot}ZH_2O$$

where in the abov formula, M represents sodium, calcium, potassium, barium, strontium, n represents the atomic value of the metal ion, and X, y, and Z are coefficients. Many different types of zeolite with different composition ratios, pore diameters, and specific surface areas, etc., are known.

However, it is necessary for the zeolite used in the present invention to contain at least one metal ion selected from silver, copper, and zinc, in a location where ion exchange can be performed (M in the above-mentioned general formula) in a natural or synthetic zeolite comprised of an aluminosilicate.

Furthermore, it is desirable for the above-mentioned specific zeolite used in the present invention to have a specific surface area in the range of 150-1000 m^2/g. A cosmetic material for hair containing the above-mentioned zeolite has superior antibacterial properties (bactericidal action), antidandruff, anti-itching properties, and provides easy combing and a great texture.

For example, the above-mentioned specific fine particulate zeolite used in the present invention can be produced by the method described below.

When one stirs a mixture produced by adding a silver salt solution (for example, silver nitrate solution), copper salt solution (for example, copper sulfate solution), or zinc salt solution (for example, zinc chloride solution) with a specific concentration with a zeolite containing a sodium ion for which ion exchange can be carried out with a silver ion, copper ion or zinc ion, for example, zeolite A (the composition is $0.94Na_2O{\cdot}Al_2O_3{\cdot}1.92SiO_2{\cdot}XH_2O$), zeolite X (the composition is

$0.99Na_2O \cdot Al_2O_3 \cdot 2.55SiO_2 \cdot XH_2O$), or zeolite Y (the composition is $1.14Na_2O \cdot Al_2O_3 \cdot 4.90SiO_2 \cdot XH_2O$) at ambient temperature, and ion-exchange reaction is carried out, and the sodium ions which are contained on the above-mentioned zeolite are exchanged with silver ions, copper ions, or zinc ions (silver zeolite, copper zeolite, or zinc zeolite is produced). The above-mentioned ion exchanged zeolite is filtered, then, it is washed with water to remove excess metal ions (metal salt), followed by drying and pulverization, and the above-mentioned specific fine particulate zeolite that can be used in the present invention is produced. For examples of zeolites that can be used for the ion-exchange treatment, the above-mentioned zeolite A, zeolite X, zeolite Y, etc., are suitable, and natural mordenite, chabazite, etc., can be used as well.

The concentration of the above-mentioned metal salt solution used for the ion exchange for the zeolites containing the above-mentioned sodium ions is 0.3 mol [sic; 0.3M] or less (0.1 mol or less is especially desirable) in a silver salt solution (silver nitrate solution), 0.05 mol or less in a copper salt solution (copper sulfate solution), and 2-3 mol or less in a zinc salt solution (zinc chloride solution).

The amount of metal included in the zeolite (absolute dry standard) containing the above-mentioned metal ions used in the present invention is 30 wt% or less for silver, preferably 0.001-5 wt%, and 35 wt% or less for copper or zinc; a range of 0.01-15 wt% is preferable. The average particle diameter of the above-mentioned specific fine particulate zeolite used in the present invention is 2 μm or less, and when the maximum particle

diameter is 10 μm or less, it can be easily mixed with the cosmetic material, and it is desirable from the standpoint of the above-mentioned effect.

The above-mentioned specific fine particulate zeolite used in the present invention is safe for humans, skin irritation does not occur, and when the skin irritation tests described below based on the Draize test were performed, the skin irritation level for animals and humans was 0 in both cases, which confirms the absence of skin irritation. (Draize, J. H., Food and Drug Administration of the United States, Appraisal of Safety of Chemicals in Foods, Drugs and Cosmetics, 46(1959), Texas State Department of Health, Austin)

The cosmetic material for hair of the present invention includes shampoos, hair rinses, hair conditioners, hair creams, hair lotions, hair milks, and hair oils, and is used as a general term that represents all of these.

The mixing ratio of the above-mentioned specific fine particulate zeolite of the present invention for the cosmetic material for hair is in the range of 0.001-50 wt% of the weight of the composition (the total weight of the formulation components); 0.1-20 wt% is preferable.

Some of the features of the cosmetic material for hair of the present invention are described below.

(1) The material has long-lasting effectiveness against *Staphylococcus epidermidis*, etc., which are present on the scalp at all times, and effectively prevents formation of dandruff and itching of the scalp.

(2) The material easily absorbs the decomposition products of the fatty components on the scalp, and removes the cause of dandruff and itching of the scalp.

(3) The above-mentioned fine particulate zeolite of the present invention is easily adsorbed by the hair, and improves combing and texture.

In the following, application examples are explained.

It should be noted that "parts" in the application examples represent parts by weight and "%" refers to wt%. Furthermore, test methods used for evaluation of the antibacterial properties, combing, tactile test (hair texture, antidandruff effect, and anti-itching effect), etc., are as explained below.

1. Antibacterial test

(1) Production of the bacterial preculture

Staphylococcus epidermidis, which is present on the scalp at all times, was used, and a culture was produced by shaking in SCD broth (culture medium) at 32°C for 48 h.

(2) Production of samples

Each cosmetic material sample was adjusted to 10% in the SCD broth (culture medium).

(3) Test

10 mL of the sample and 0.1 mL of the above-mentioned culture were poured into a 500-mL conical flask while mixing. Shaking culture was carried out at 32°C for said mixture, and after 48 h, the number of bacteria in 1 mL of each test solution was counted by the plate colony counter method (32°C, 72 h, SCD agar culture medium), and evaluated.

(4) Evaluation

The germ kill ratio was obtained using the mathematical equation shown below.

germ kill ratio (%) = 100 - (number of live bacteria at the time sample was added (log [sic]/mL·2 days)] / (number of live bacteria at the time when sample was not added (log/ml·2 days)) x 100

The higher the above value, the higher the antibacterial effect.

2. Combing effect (coefficient of friction) for the hair test

In order to examine the effect on combing of the treated hair, 4 g of human hair were treated with 0.5 g of the sample cosmetic material, and the coefficient of friction was measured by the ladder [transliteration] system friction measuring device.

It should be noted that the lower the above-mentioned value, the better the combing effect.

3. Sensor test

Each test shown below was performed by 10 male volunteers, and 10 female volunteers, for a total of 20 panelists.

(1) Texture

The softness of the hair before and after treatment with the combing test was compared. The number shows the number of peopl who observed softness after the treatment among the 20 volunteers.

(2) Antidandruff and anti-itching effect

The sample cosmetic material was used once a day for a 2-week continuous test. Formation of dandruff and itching before

and after the test were compared, and when the formation of dandruff was reduced after the test duration, it was defined that the antidandruff effect was observed, and in the same manner, when itching was absent, the anti-itching effect was observed. The numbers represent the number of volunteers who observed the above-mentioned effects.

Application Example 1

(1) Production of the silver zeolite Y used in the present invention

500 mL of 1/10M silver nitrate solution were added to 250 g of dry zeolite Y (the composition is $1.14Na_2O{\cdot}Al_2O_3{\cdot}4.90SiO_2{\cdot}XH_2O$) (the particle diameter is 0.6 μm, the specific surface area is 908 m^2/g), which is the zeolite raw material, the mixture produced was maintained at room temperature for 5 h while stirring, and ion exchange was performed. The silver zeolite Y produced as a result of said ion-exchange process was filtered; subsequently, it was washed with water to remove excess silver ion.

Then, the washed silver zeolite Y was dried at 100-105°C and pulverized, and a fine particulate silver zeolite Y was produced. The silver content in the dried silver zeolite Y produced was 2.08%, the specific surface area was 875 m^2/g, and the particle diameter was an average of 0.6 μm.

(2) Production of hair cream of the present invention

A dispersion (80°C) produced by uniformLy dispersing 0.1 part of the silver zeolite Y produced above in (1) in 76.9 parts of water were added to a uniform molten material (80°C) comprised of 5 parts of cetyl alcohol, 10 parts of liquid paraffin, 3 parts of polyoxyethylene (EO = 5 mol) cetyl ether, 2 parts of monoglyceride stearate, and 3 parts of lanolin fatty acid isopropyl ester, and emulsified, cooled to 30°C, and the hair cream of the present invention was produced.

(3) The effect (performance) of the hair cream of the present invention produced above in (2) was evaluated by the test method described above.

The results indicate that the coefficient of friction tested by the combing method was 0.144, and the results obtained were very good.

18 volunteers out of 20 claimed that the texture after the tactile test was good, 17 volunteers out of 20 claimed that the antidandruff performance was good, and 18 volunteers out of 20 claimed that the anti-itching performance was good.

Furthermore, the antibacterial effect of the hair cream was 100% in terms of the germ killing ratio.

Comparative Example 1

The silver zeolite Y used in Application Example 1 (3) was not used, and 77 parts of water were used, and the test was performed as in Application Example 1, and a comparison (control)

hair cream was produced. The coefficient of friction of the hair of the comparison produced was 0.233 and combing performance was poor. Furthermore, only 2 volunteers out of 20 claimed that the texture was improved after the tactile test, and 1 volunteer out of 20 claimed that the antidandruff effect was good, and 2 volunteer out of 20 claimed that the anti-itching properties were good. The antibacterial effect of the hair cream produced was 0% in terms of the germ kill ratio.

Comparative Example 2

Instead of the silver zeolite Y of the present invention, the zeolite raw material zeolite Y used in Application Example 1 (1) was used, and the test was performed as in Application Example 1 (3), and a comparison hair cream was produced.

The coefficient of friction of the hair of the comparison produced was 0.200 and combing effect was poor. Furthermore, only 8 volunteers out of 20 claimed that the texture was improved after the sensory test, and 5 volunteers out of 20 claimed that the antidandruff effect was good, and 6 volunteers out of 20 claimed that the anti-itching properties were good. The antibacterial effect of the hair cream produced was 0% in terms of the germ kill ratio.

Application Example 2

(1) Production of a copper zeolite Y used in the present invention

Instead of 1/10M silver nitrate solution, 1 L of 1/20M copper sulfate solution was produced, ion exchange was carried out as in Application Example 1 (1), and a fine particulate copper zeolite Y was produced. The copper content in the dried product of the copper zeolite Y produced was 8.70%, the specific surface area was 903 m^2/g, and the average particle diameter was 1.6 μm.

(2) Hair cream of the present invention and the performance of the product

Instead of the silver zeolite Y described above, said copper zeolite Y was used, and a test was performed as in Application Example 1 (2), and a hair cream of the present invention was produced. The coefficient of friction of the hair treated with the hair cream produced was 0.160, and combing was very good. Furthermore, 19 volunteers out of 20 claimed that the texture after the sensory test was good, 18 volunteers out of 20 claimed that the antidandruff performance was good, and 18 volunteers out of 20 claimed that the anti-itching performance was good. Furthermore, the antibacterial effect of the hair cream was 98% in terms of the germ kill ratio.

Application Example 3

(1) Production of zinc zeolite Y used in the present invention

Instead of 1/10M silver nitrate solution, 1 L of 2M zinc chloride was used, ion exchange was carried out as in Application Example 1 (1), and a fine particulate zinc zeolite Y was produced. The zinc content in the dried product of the zinc zeolite Y produced was 10.9%, the specific surface area was 846 m^2/g, and the average particle diameter was 0.6 μm.

(2) Production of a hair cream of the present invention and the performance of the product

Instead of silver zeolite Y, said zinc zeolite Y was used, and a test was performed as in Application Example 1 (2), and a hair cream of the present invention was produced.

The coefficient of friction of the hair treated with the hair cream produced was 0.161, and combing performance was very good. 18 volunteers out of 20 claimed that the texture after the tactile test was good, 19 volunteers out of 20 claimed that the antidandruff performance was good, and 18 volunteers out of 20 claimed that the anti-itching performance was good. Furthermore, the antibacterial effect of the hair cream was 100% in terms of the germ kill ratio.

Application Example 4

1 part of copper zeolite Y produced in Application Example 2 (1), 75 parts of water, 15 parts of polyoxyethylene (EO = 3 mol) lauryl ether, 2 parts of sodium dodecylsulfate, and 7 parts of coconut oil fatty acid diethanolamide were mixed under stirring, and a hair shampoo of the present invention was produced.

The coefficient of friction of the hair treated with the hair cream produced was 0.182, and combing performance was very good. 18 volunteers out of 20 claimed that the texture after the tactile test was good, 19 volunteers out of 20 claimed that the antidandruff performance was good, and 18 volunteers out of 20 claimed that the anti-itching performance was good. Furthermore, the antibacterial effect of the hair cream was 100% in terms of the germ kill ratio.

Comparative Example 3

The above-mentioned copper zeolite Y was omitted and 76 parts of water were used, the test was performed as in Application Example 4, and a comparison (control) hair shampoo was produced. The coefficient of friction of the hair of the comparison hair shampoo was 0.243 and combing performance was poor. Furthermore, only 3 volunteers out of 20 claimed that the texture was improved after the tactile test, and 1 volunteer out of 20 claimed that the antidandruff effect was good, and 2 volunteers out of 20 claimed that the anti-itching properties were good. The antibacterial effect of the hair cream produced was 0% in terms of the germ kill ratio.

Application Example 5

(1) Production of a zinc zeolite Y used in the present invention

Instead of zeolite Y, zeolite X (the composition was $0.99Na_2O \cdot Al_2O_3 \cdot 2.55SiO_2 \cdot XH_2O$) (the particle diameter is 1.6 μm, the specific surface area is 838 m^2/g) was used, and ion exchange was carried out as in Application Example 3 (1), and a fine particulate copper zeolite X was produced. The zinc content in the dried product of the zinc zeolite X produced was 0.82%, the specific surface area was 826 m^2/g, and the average particle diameter was 1.6 μm.

(2) Hair rinse of the present invention and performance of the product

5 parts of zinc zeolite X produced above in (1), 71 parts of water, 1 part of stearyltrimethylammonium chloride, 1 part of liquid paraffin, 0.5 parts of lanolin fatty acid isopropyl ester, 2 parts of cetyl alcohol, 1 part of polyoxyethylene (EO = 5 mol) oleyl ether, 0.5 part of stearic acid monoglyceride, and 8 parts of glycerol were mixed with stirring, and a hair rinse of the present invention was produced. The coefficient of friction of the hair treated with the hair rinse produced was 0.129, and combing performance was very good. Furthermore, 20 volunteers out of 20 claimed that the texture after the tactile test was good, 19 volunteers out of 20 claimed that the antidandruff performance was good, and 18 volunteers out of 20 claimed that

the anti-itching performance was good. Furthermore, the antibacterial effect of the hair cream was 100% in terms of the germ kill ratio.

Comparative Example 4

The zinc zeolite X produced in Application Example 5 (1) was omitted, and 76 parts of water were used, and the test was performed as in Application Example 5 (2), and a comparison (control) hair rinse was produced. The coefficient of friction of the hair of the comparison produced was 0.171 and combing performance was poor. Furthermore, only 8 volunteers out of 20 claimed that the texture was improved after the tactile test, and 4 volunteers out of 20 claimed that the antidandruff effect was good, and 2 volunteers out of 20 claimed that the anti-itching properties was good. The antibacterial effect of the hair cream produced was 40% in terms of the germ kill ratio.

Application Example 6

(1) Production of silver zeolite A used in the present invention

Instead of the zeolite Y used in Application Example 1 (1), zeolite A (the composition was $0.94Na_2O \cdot Al_2O_3 \cdot 1.92SiO_2 \cdot XH_2O$) (the particle diameter is 1.1 μm, the specific surface area is 664 m^2/g)was used, and ion exchange was performed as in Application Example 1 (1), and a fine particulate silver zeolite A was produced. The zinc content in the dried product of the

silver zeolite A produced was 2.39%, the specific surface area was 629 m^2/g, and the average particle diameter was 1.1 μm.

(2) Hair lotion of the present invention and the performance of the product

0.1 part of silver zeolite A produced above in (1), 43.4 parts of water, 50 parts of ethyl alcohol, 0.5 part of L-menthol, 5 parts of glycerol, and 1 part of perfume were mixed with stirring, and a hair lotion of the present invention was produced.

The coefficient of friction of the hair treated with the hair lotion produced was 0.188, and combing performance was very good. Furthermore, 18 volunteers out of 20 claimed that the texture after the tactile test was good, 19 volunteers out of 20 claimed that the antidandruff performance was good, and 18 volunteers out of 20 claimed that the anti-itching performance was good.

Comparative Example 5

The silver zeolite A produced in Application Example 6 (1) was omitted, and 43.5 parts of water were used, the test was performed as in Application Example 6 (2), and a comparison (control) hair lotion was produced. The coefficient of friction of the hair of the comparison hair lotion was 0.221 and combing performance was poor. Furthermore, only 2 volunteers out of 20 claimed that the texture was improved after the tactile test, and

1 volunteer out of 20 claimed that the antidandruff effect was good, and 1 volunteer out of 20 claimed that the anti-itching properties was good.

Application Example 7

The mixing ratio of the silver zeolite Y produced in Application Example 1 (2) was changed to the ratios shown in Table I below, and performance of hair creams produced were examined. The results obtained are shown in Table I. As is clear from the test results of Table I, the mixing ratio of silver zeolite Y of 0.001-50 wt% of the weight of the composition (total weight of the formulation components) is suitable, and 0.1-20 wt% is further desirable.

Table I

① 配合率 (%)	② 抗菌性試験 (死滅率) (%)	③ 櫛通り試験 (動マサツ係数)	④ 官能試験※ ⑤ 良い合	フケ防止効果 ⑥	かゆみ防止効果 ⑦
0	0	0.238	5人	1人	2人
0.0001	20	0.207	7	5 ⑧	6
0.001	80	0.175	15	12	14
0.01	100	0.164	16	16	15
0.1	100	0144	18	17	18
1.0	100	0.155	19	18	20
10.0	100	0.148	18	19	19
20.0	100	0.159	18	17	18
50.0	100	0.197	16	16	16
60.0	100	⑨ 測定不能	粘土状のヘアークリームを生成し、毛髪の処理が不可能 ⑩		

⑪ ※ パネラー20人中、良好であると答えた人数を示す。

Key: 1 Mixing ratio (%)
2 Antibacterial test (germ kill ratio) (%)
3 Combing performance (coefficient of friction)
4 Tactile test
5 Texture
6 Antidandruff effect
7 Anti-itching effect
8 People
9 Measurement not possible
10 A clay-like hair cream was produced, and treatment of the hair with the product was impossible.
11 * Number of people answered "good" among 20 volunteers.